

# SMEARING FORMULAS FOR DENSITY MATRICES

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We report on the development of a systematic variational perturbation theory for the euclidean path integral representation of the density matrix based on new smearing formulas for harmonic correlation functions. As a first application, we present the lowest-order approximation for the radial distribution function of an electron in a hydrogen atom.

## 1 Introduction

Quantum statistical free energies can be calculated to any desired accuracy with the help of variational perturbation theory<sup>1,2</sup>. This is a systematic generalization of an earlier rough variational approach<sup>3,4</sup> based on the Jensen-Peierls inequality. The approximation consists of an optimized expansion, in which each term can be expressed via a simple smearing formula<sup>5</sup> applied to powers of the interaction, which can be polynomial as well as nonpolynomial.

In Sect. 2 we sketch the extension of this theory to density matrices, thus enabling us to calculate very accurately local statistical properties of a quantum mechanical system at all temperatures and coupling strengths. The corresponding smearing formulas are derived in Sect. 3 and applied in Sect. 4 to obtain the lowest-order approximation for the density distribution of a Coulomb system.

## 2 Variational Perturbation Theory for Density Matrices

Variational perturbation expansions for the free energy approximate arbitrary quantum statistical systems by optimized local perturbation expansions around harmonic systems with different trial frequencies. The optimization is performed separately for each path average  $x_0 = \int_0^{\hbar\beta} x(\tau)/\hbar\beta$ . This ensures a rapid convergence of such expansions at higher temperatures by removing the fluctuations of  $x_0$  which diverge linearly with the temperature. The fluctuations of  $x_0$  are accounted for at the end by an ordinary integral. Since these fluctuations probe, at higher temperatures, the entire potential, they must be done numerically, and the fact that this is always possible with high accuracy is one of the reasons for the quality of the approximations<sup>2</sup>.

When applying variational perturbation theory to density matrices, the special role of the  $x_0$ -fluctuations disappears since  $x_0$  remains always close to some average of the fixed endpoints of the paths. Then  $x_0$  may be treated perturbatively<sup>6</sup> together with the other Fourier components of the paths. We may therefore directly look for an optimized perturbation expansion of the path integral for the unnormalized density matrix

$$\tilde{\rho}(x_a, x_b) = \int_{x_a, 0}^{x_b, \hbar\beta} \mathcal{D}x \exp \left\{ -\frac{1}{\hbar} \mathcal{A}[x] \right\}, \quad (1)$$

where  $\beta = 1/k_B T$  and  $\mathcal{A}$  is the euclidean action. In order to obtain a variational approximation, we divide the full action into a harmonic trial action with center  $x_{\min} = x_{\min}(x_a, x_b)$  and frequency  $\Omega = \Omega(x_a, x_b, x_{\min})$ . Denoting the trial action by  $\mathcal{A}_{\Omega, x_{\min}}$ , the remainder  $\mathcal{A}_{\text{int}} = \mathcal{A} - \mathcal{A}_{\Omega, x_{\min}} = \int_0^{\hbar\beta} d\tau V_{\text{int}}(x(\tau))$  is treated as a perturbation. The result can be written as an exponential of a cumulant expansion (cumulants being indicated by subscript  $c$ )

$$\tilde{\rho}(x_a, x_b) = \tilde{\rho}_{\Omega, x_{\min}}(x_a, x_b) \times \exp \left\{ -\frac{1}{\hbar} \langle \mathcal{A}_{\text{int}}[x] \rangle_{\Omega, x_{\min}, c}^{x_a, x_b} + \frac{1}{2\hbar^2} \langle \mathcal{A}_{\text{int}}^2[x] \rangle_{\Omega, x_{\min}, c}^{x_a, x_b} - \dots \right\}. \quad (2)$$

The prefactor  $\tilde{\rho}_{\Omega, x_{\min}}(x_a, x_b)$  is the unnormalized density matrix of the displaced euclidean harmonic propagator. The connected correlation functions in the exponent of (2) consist of the harmonic expectation values

$$\langle \mathcal{A}^n[x] \rangle_{\Omega, x_{\min}}^{x_a, x_b} = [\tilde{\rho}_{\Omega, x_{\min}}(x_a, x_b)]^{-1} \times \int_{x_a, 0}^{x_b, \hbar\beta} \mathcal{D}x \prod_{k=1}^n \left[ \int_0^{\hbar\beta} d\tau_k V_{\text{int}}(x(\tau_k)) \right] \exp \left\{ -\frac{1}{\hbar} \mathcal{A}_{\Omega, x_{\min}}[x] \right\}. \quad (3)$$

Truncating the series (2) after the  $N$ th term, we find the approximation  $\tilde{\rho}_N(x_a, x_b; \Omega, x_{\min})$  to the euclidean propagator (1). As the exact propagator  $\tilde{\rho}(x_a, x_b)$  does not depend on the variational parameters, we expect the best approximation  $\tilde{\rho}_N(x_a, x_b; \Omega, x_{\min})$  to depend minimally on them. To determine the optimal values  $\Omega^N$  and  $x_{\min}^N$ , we thus solve the extremality conditions  $\partial \tilde{\rho}_N(x_a, x_b; \Omega, x_{\min}) / \partial \Omega = 0$  and  $\partial \tilde{\rho}_N(x_a, x_b; \Omega, x_{\min}) / \partial x_{\min} = 0$ . If no extremal point is found, higher derivatives can be used<sup>2</sup>. The associated density matrix  $\rho_N$  is found by normalizing  $\tilde{\rho}_N$ :

$$\rho_N(x_a, x_b) = \frac{\tilde{\rho}_N(x_a, x_b; \Omega^N(x_a, x_b, x_{\min}(x_a, x_b)), x_{\min}^N(x_a, x_b))}{\int_{-\infty}^{+\infty} dx \tilde{\rho}_N(x, x; \Omega^N(x, x, x_{\min}^N(x, x)), x_{\min}^N(x, x))}. \quad (4)$$

### 3 Smearing Formula

To determine the expectation values (3), we proceed as in Ref. <sup>7</sup>, and introduce the Fourier identity

$$\mathcal{A}_{\text{int}}[x] = \int_0^{\hbar\beta} d\tau \int_{-\infty}^{+\infty} dz V_{\text{int}}(z) \int_{-\infty}^{+\infty} \frac{dk}{2\pi} e^{ikz} \exp \left\{ \frac{1}{\hbar} \int_0^{\hbar\beta} d\tau' j(k, \tau') x(\tau') \right\} \quad (5)$$

with the current  $j(k, \tau') = -i\hbar k \delta(\tau - \tau')$ . Thus the expectation values (3) are reduced to path integrals for the euclidean harmonic propagator of exponentials of the fluctuating variables. But harmonic expectation values of products of exponentials can be written as products of exponentials of pair correlation functions as a simple generalization of Wick's rule (the simplest well-known application of this being the calculation of the Debye-Waller factor for harmonic phonons). Performing the remaining Gaussian integrals we obtain directly the smearing formula

$$\begin{aligned} \langle \mathcal{A}_{\text{int}}^n[x] \rangle_{\Omega, x_{\text{min}}}^{x_a, x_b} &= \prod_{k=1}^n \left[ \int_0^{\hbar\beta} d\tau_k \int_{-\infty}^{+\infty} dz_k V_{\text{int}}(z_k + x_{\text{min}}) \right] \\ &\times \frac{1}{\sqrt{(2\pi)^n \det G}} \prod_{k,l=1}^n \exp \left\{ -\frac{1}{2} [z_k - x_{\text{cl}}(\tau_k)] G_{kl}^{-1}(\tau_k, \tau_l) [z_l - x_{\text{cl}}(\tau_l)] \right\}, \end{aligned} \quad (6)$$

where  $x_{\text{cl}}(\tau)$  is the classical harmonic path and  $G$  denotes the  $n \times n$ -matrix of harmonic Green functions

$$G_{kl}(\tau_k, \tau_l) = \frac{\hbar}{2M\Omega} \frac{\cosh \Omega(|\tau_k - \tau_l| - \hbar\beta) - \cosh \Omega(\tau_k + \tau_l - \hbar\beta)}{\sinh \hbar\beta\Omega}. \quad (7)$$

An important advantage of the smearing formula (6) over the conventional diagrammatic perturbation expansions is that it also allows to calculate correlation functions for nonpolynomial problems.

### 4 Electron Distribution in Hydrogen Atom

As an example, consider the electron distribution in the hydrogen atom for different temperatures shown in Fig. 1. Denoting by  $r_a = |\mathbf{r}_a|$  the distance of the electron from the proton, one usually plots the so-called *pair distribution function*  $g_1(\mathbf{r}_a)$ , which is equal to  $(2\pi\beta)^{3/2}$  times the unnormalized density  $\tilde{\rho}_1(\mathbf{r}_a, \mathbf{r}_a)$ . Our result is better than an earlier approximation obtained from a simple smearing of the effective classical potential of the system <sup>2,9</sup>.

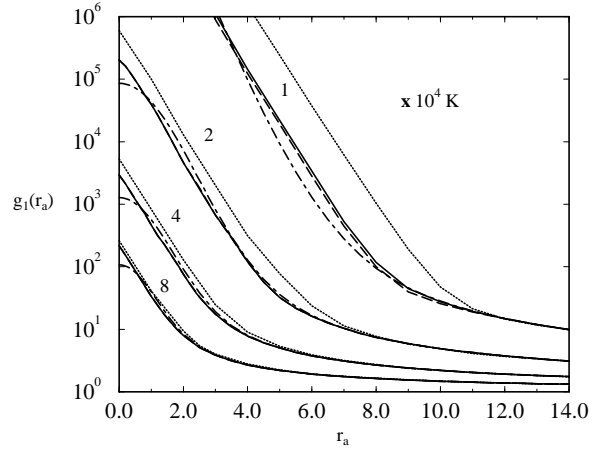


Figure 1. Radial distribution function for an electron in a hydrogen atom. The first-order results obtained with isotropic (dashed curves) and anisotropic (solid) variational perturbation theory are plotted against Storer's results<sup>8</sup> (dotted) and an earlier curve obtained from the first-order effective classical potential<sup>2,9</sup> (dash-dotted).

## Acknowledgments

The work of one of us (M.B.) is supported by the Studienstiftung des deutschen Volkes.

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